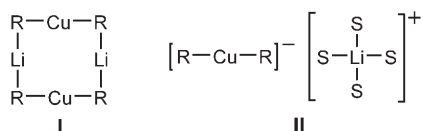


Structural Characterization of Magnesium Organocuprates Derived from Grignard Reagents: Cu^I-Based Inverse Crown Ethers**

Roberta Bomparola, Robert P. Davies,* Stefan Hornauer, and Andrew J. P. White

Organocuprates are excellent reagents for the formation of carbon–carbon bonds and have been used extensively in synthetic methodology since the 1960s.^[1] They are typically formed in situ through the reaction of either an organolithium or magnesium Grignard reagent with a copper(I) salt. The resting state and also reactive form of lithium organocuprates in nonpolar or weakly coordinating solvents, such as Et₂O, is now commonly accepted to be a dimeric contact ion pair (CIP) species **I**. In more strongly coordinating solvents, such

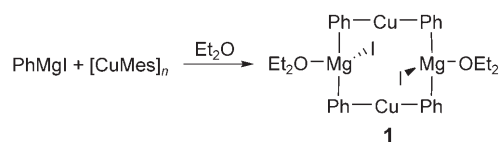


as THF, a less reactive solvent-separated ion pair (SSIP) **II** is predominant.^[2,3]

However, in stark contrast to recent advances in the understanding of lithium organocuprates, the structures of the equally ubiquitous magnesium organocuprates derived from Grignard reagents remain unexplored. To our knowledge, [Cu₄MgPh₆(OEt₂)], prepared by the treatment of CuBr with MgPh₂ in Et₂O, is the only structurally characterized example of a magnesium organocuprate,^[4] although the aryl copper magnesium arenethiolate [[Cu₄Mes₄]{μ-SAr}₂{MgSAr}₂] (Mes = 2,4,6-Me₃C₆H₂; Ar = 2-Me₂NCH(Me)C₆H₄)—formed from the self-assembly of (CuSAr)₃ and MgMes₂—has also been proposed as a possible active species in Mg-catalyzed cuprate addition reactions.^[5,6] Herein, we present the first structural determination of magnesium organocuprates derived from Grignard reagents. Cu^IMes was employed as the organocopper starting material in all reactions because of its high thermal stability and previous use in the preparation of stable lithium homo- and heteroamidocuprates.^[7,8]

The treatment of CuMes with PhMgI in Et₂O/toluene gave a clear solution from which colorless crystals of

[[{Ph₂Cu}{Mg(OEt₂)I}]₂] (**1**) were obtained (Scheme 1). X-ray crystallography^[9] showed **1** to exist as a centrosymmetric dimer consisting of two cuprate [Ph–Cu–Ph][−] anions con-



Scheme 1. Synthesis of **1**.

nected by Et₂O-solvated (MgI)⁺ monocations (Figure 1). The Mg centers in **1** are approximately tetrahedral with the Mg-coordinated iodide centers lying one above and one below the

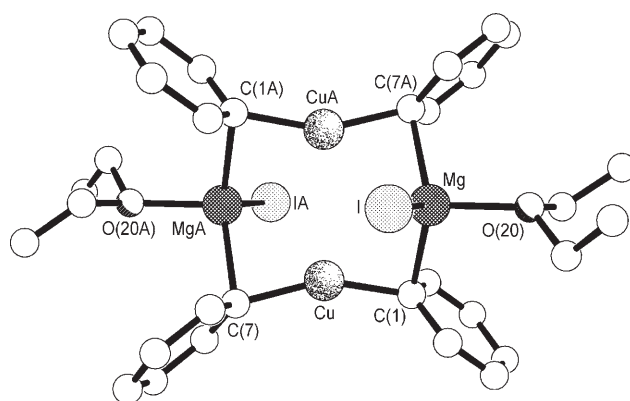


Figure 1. The molecular structure of the C₂-symmetric complex **1**.

central eight-membered Cu₂Mg₂C₄ ring (Mg–I 2.7046(10) Å). It is salient that the structure is therefore isostructural to the previously reported lithium diphenylcuprate [[{Ph₂Cu}{Li(OEt₂)}]₂],^[10] with the lithium cations formally replaced by (MgI)⁺ monocations. Thus, we believe these results provide the first experimental evidence that magnesium Grignard diorganocuprates are able to form analogous CIP structures to those (of type **I**) now well-established for lithium diorganocuprates.

The phenyl groups in **1** bridge the Cu and Mg centers to form asymmetric three-center, two-electron (3c–2e) Mg–C–Cu bonds. The Cu–C_{ipso} distances in **1** (Cu–C(7) 1.939(3), Cu–C(1) 1.945(3) Å) are comparable to those in [[{Ph₂Cu}{Li(OEt₂)}]₂]^[10] and other lithium diaryl cuprates (1.906(5)–1.948(3) Å),^[10–12] all of which contain analogous 3c–2e Cu–C–Li bonds. However, at 156.97(13)°, the C–Cu–C bond angle in **1** is less obtuse than the equivalent angles in these lithium

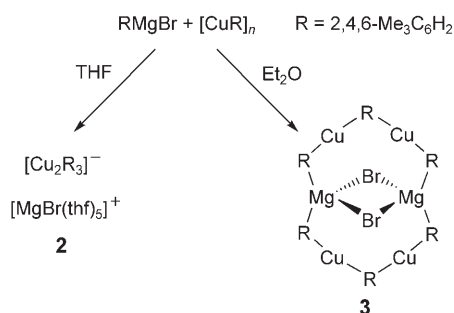
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diaryl cuprates (mean angle: 162.8°).^[10–12] Furthermore, the Mg–C distances in **1** (Mg–C(1) 2.261(3), Mg–C(7A) 2.290(3) Å) are significantly shorter than those in the only other magnesium organocuprate studied, [Cu₄MgPh₆(OEt₂)] (mean Mg–C distance: 2.35(1) Å), in which the Mg center bridges three phenyl groups.^[4]

Although crystalline **1** was obtained in moderate yield (31 % with respect to PhMgI) from the reaction in Scheme 1, the fate of the Mes ligand remained unknown, and it was apparent that at least one other product must also be formed in the reaction mixture. We envisaged initially that this product could take the form of an analogous [(Mes₂Cu)–(MgI)]₂ dimer; however, NMR spectroscopic experiments to investigate this possibility proved inconclusive. To probe the identity of this additional product, the reaction was replicated with MesMgBr as the Grignard reagent (Scheme 2).



Scheme 2. Synthesis of **2** and **3**.

The treatment of CuMes with MesMgBr in THF/toluene gave a white powder, which was recrystallized from hot toluene to give colorless crystals of [Cu₂Mes₃][−][MgBr(thf)₅]⁺ (**2**). These crystals were characterized by X-ray crystallography (Figure 2).^[13] Complex **2** can be considered most simply as a SSIP consisting of a magnesium-based cation and copper aryl anion. The structure of **2** is therefore directly comparable to the structure in THF of lithium diorganocuprates, which also adopt a SSIP arrangement under such conditions (see **II**), except with the surprising replacement of the mononuclear [R₂Cu][−] cuprate anion with a dinuclear [R₃Cu₂][−] unit.

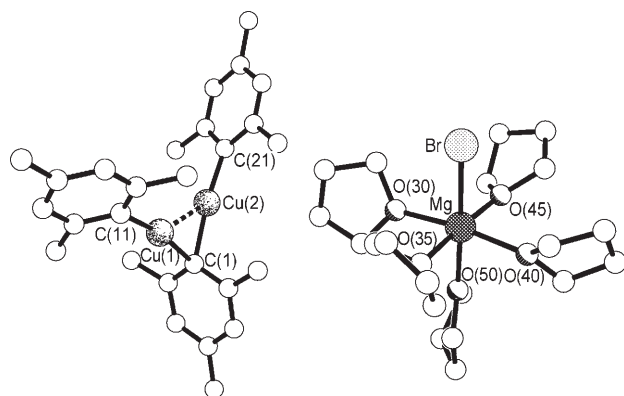


Figure 2. The molecular structure of **2**.

The cation in **2** is unexceptional: It contains an octahedral Mg center coordinated to five THF molecules and one bromide atom (Mg–Br 2.586(3) Å). However, the dinuclear [Mes₃Cu₂][−] anion is unique, with two terminal Mes groups, which can be considered to form short 2c–2e bonds with the Cu centers (Cu(1)–C(11) 1.923(8), Cu(2)–C(21) 1.925(8) Å), and one Mes group, which bridges both Cu centers through an approximately symmetric 3c–2e Cu–C–Cu bond to give longer Cu–C distances (Cu(1)–C(1) 2.020(7), Cu(2)–C(1) 2.003(8) Å). Structures of the type [Cu₂R₃][−] were not known previously in organocopper chemistry, although the organoiodocuprate [2,6-Mes₂H₃C₆Cu₂I₂][−] does have a similar arrangement, with iodine atoms instead of organo groups in the terminal positions.^[14] The bond angles in **2** at Cu(1) and Cu(2) are 168.0(3) and 171.0(3)°, respectively, and the Cu–C–Cu angle at the bridging *ipso* C atom is 75.1(3)°. This arrangement gives rise to an intramolecular Cu···Cu distance of 2.4515(14) Å. Although this Cu···Cu contact is very short, it does not imply the presence of any significant Cu–Cu bonding interactions: Recent computational studies on the nature of any possible d¹⁰–d¹⁰ interactions between Cu^I centers showed that such interactions between Cu^I centers of similar charge are likely to be weak or nonexistent.^[15]

Repetition of the reaction between CuMes and MesMgBr in the less strongly coordinating medium Et₂O/toluene gave a different product: [Cu₄Mg₂Mes₆Br₂] (**3**; Scheme 2). X-ray crystallographic studies^[16] revealed the crystals of **3** to contain two structurally identical but independent C_i-symmetric complexes **3a** and **3b** in the asymmetric unit (see the Supporting Information), one of which is shown in Figure 3. Complex **3** adopts a CIP arrangement, formally an aggrega-

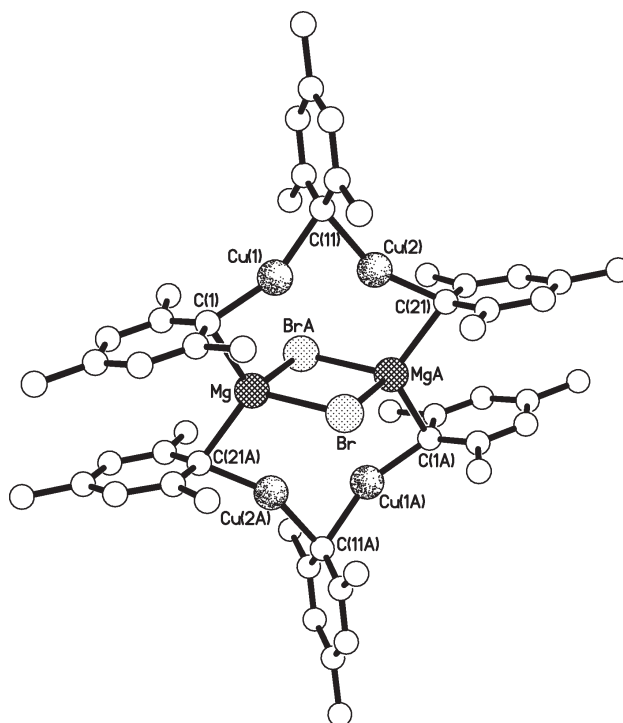


Figure 3. The molecular structure of **3a**, one of the two crystallographically independent C_i-symmetric complexes present in the crystals of **3**.

tion of two $(\text{MgBr})^+$ cations and two $[\text{Cu}_2\text{Mes}_3]^-$ anions—that is, of the same structural units present in the SSIP complex **2**. The structures of **2** and **3** therefore hint at close parallels between the behavior of lithium organocuprates and Grignard reagent derived magnesium organocuprates, whereby CIP structures (**1** and **3**) are favored in weakly coordinating solvents, such as Et_2O , and SSIP structures (**II** and **2**) are favored in more strongly coordinating solvents, such as THF.

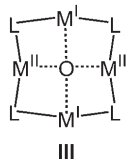
The Mg centers in **3** are approximately tetrahedral and form a central four-membered Mg_2Br_2 ring with the two bromine atoms, with the Mg–Br bond distances in the range 2.5683(9)–2.5735(9) Å (mean distance: 2.5707 Å). The Mg–C distances are in the range 2.260(2)–2.274(2) Å (mean distance: 2.268 Å); thus, the Mg–C bonds are comparable in length to those in **1**.

Two different types of mesityl groups are present in **3**: The first type bridges two Cu^{I} atoms symmetrically to give a 3c–2e bond with Cu–C distances in the range 1.981(2)–2.002(2) Å (mean distance: 1.994 Å). These distances are similar to the Cu–C distances in the anion of **2**. However, the Cu–C_{ipso}–Cu angles (77.56(9), 78.40(9)°) are less acute than the equivalent angle in **2**, thus resulting in a longer Cu···Cu distance (2.5044(6), 2.5136(5) Å). The second type of mesityl group bridges a Mg and a Cu center asymmetrically to form shorter Cu–C contacts (1.955(2)–1.971(2) Å; mean distance: 1.964 Å). The bond angles at the Cu centers in **3** lie in the range 154.23(9)–158.72(9)° (mean angle: 156.63°) and thus are less obtuse than the C–Cu–C angles in **2**, presumably as a result of the steric requirements of the central Mg_2Br_2 ring.

Complex **3** can also be considered as a dimer similar to **1**, but with the $[\text{Ph}_2\text{Cu}]^-$ units in **1** replaced by $[\text{Mes}_3\text{Cu}_2]^-$ units. The difference in the composition of these cuprate anions in **1** and **3** can be explained by the increased steric requirements of the Mes group over that of the Ph group. Thus, the formation of a possible dimeric $[(\text{Mes}_2\text{Cu})(\text{MgBr})_2]$ structure is prevented as a result of the steric clash between *ortho* CH_3 groups on the Mes ring and bromine atoms. Lithium dimesitylcuprate, however, has been shown to adopt a dimeric $[(\text{Mes}_2\text{Cu})\text{Li}]_2$ motif, as Li^+ is considerably less sterically demanding than $(\text{MgBr})^+$.^[7]

It seems likely that the formation of **3** is also a key first step in the reaction in THF. Thus, we propose that an aggregate similar or identical to **3** is formed initially and then solvated by THF to give the SSIP **2**. This pathway would explain the observation of $[\text{Cu}_2\text{Mes}_3]^-$ anions in **2**, rather than the expected $[\text{CuMes}_2]^-$ anions.

It is also important to consider the structures of **1** and **3** in the light of recent studies on “inverse crown ether” complexes: a special class of heterobimetallic compounds typically containing dicationic eight-membered ($[\text{M}^{\text{I}}_2\text{M}^{\text{II}}_2\text{L}_4]^{2+}$) or twelve-membered macrocycles ($[\text{M}^{\text{I}}_4\text{M}^{\text{II}}_2\text{L}_6]^{2+}$), in which M^{I} is an alkali metal (Li^+ , Na^+ , K^+), M^{II} is a divalent metal (Mg^{2+} , Ca^{2+} , Zn^{2+} , Mn^{2+}), and L is an amido, alkyl, or enolato ligand.^[17–20] These macrocycles (see, for example, **III**) are named inverse crown ethers because of their ability to bind organic or inorganic anions and their topological similarity to organic crown ethers. Further-



more, the metal centers within these complexes have been observed to have a unique synergic relationship, which has resulted in the application of these complexes in some unparalleled regioselective and/or polydeprotonation reactions.^[17] In this context, **1** can be considered as an eight-membered $[\text{Cu}_2\text{Mg}_2\text{C}_4]^{2+}$ inverse crown ether and **3** as a 12-membered $[\text{Cu}_4\text{Mg}_2\text{C}_6]^{2+}$ inverse crown ether. They constitute the first examples of inverse crown ethers in which the alkali metal has been replaced formally by a transition metal (Cu^{I}). In **1**, the iodine atoms are too large to fit within the macrocycle and therefore lie directly outside the $\text{Cu}_2\text{Mg}_2\text{C}_4$ ring, whereas in **3**, the bromine atoms are present as “guest” anions to give a central Mg_2Br_2 ring similar to, for example, the Mg_2H_2 ring in the hydride-guest-anion complex $[\text{Na}_2\text{Mg}_2(\text{H})_2[\text{N}(\text{iPr})_2]_4]^{[21]}$ or the $\text{Mg}_2(\text{OnBu})_2$ ring in the alkoxo-guest-anion complex $[\text{Na}_2\text{Mg}_2(\text{OnBu})_2[\text{N}(\text{iPr})_2]_4]^{[22]}$.

In summary, the first structural characterization of magnesium organocuprates derived from Grignard reagents shows close parallels between these complexes and lithium organocuprates. In particular, both types of organocuprates adopt dimeric CIP structures in Et_2O and SSIP structures in THF. Whereas complex **1** is directly isostructural with its lithium analogue $[(\text{Ph}_2\text{Cu})\{\text{Li}(\text{OEt}_2)\}]_2$, complex **3** forms a unique larger ring system as a result of the increased steric requirements of the Mes group. Complexes **1** and **3** can also be considered as rare examples of dicationic transition-metal-containing inverse crown ethers based upon 8- and 12-membered macrocycles, respectively.

Experimental Section

All reactions were carried out under a protective nitrogen atmosphere. $\text{Cu}^{\text{I}}\text{Mes}$ was prepared according to a literature procedure.^[23]

1: A solution of $\text{Cu}^{\text{I}}\text{Mes}$ (730 mg, 4 mmol) in toluene (10 mL) was added to a solution of phenylmagnesium iodide in diethylether (0.79 M, 4.6 mL, 3.64 mmol). The mixture was stirred for 30 min at room temperature and then filtered through celite. Storage at 4 °C for 14 days yielded **1** (0.246 g, 31 % based on PhMgI) as colorless crystals suitable for X-ray crystallographic analysis. M.p.: 188–192 °C.

2: A solution of $\text{Cu}^{\text{I}}\text{Mes}$ (365 mg, 2 mmol) in toluene (5 mL) was added to a solution of mesitylmagnesium bromide in THF (0.50 M, 4.0 mL, 2 mmol) to give a white precipitate. The solvent was evaporated under reduced pressure, and the precipitate was redissolved in hot toluene (15 mL). The solution was allowed to cool to room temperature, whereupon complex **2** (0.352 g, 56 %) crystallized as colorless crystals suitable for X-ray crystallographic analysis. M.p.: 198 °C (decomp.).

3: A solution of $\text{Cu}^{\text{I}}\text{Mes}$ (365 mg, 2 mmol) in toluene (5 mL) was added to a solution of mesitylmagnesium bromide in diethyl ether (0.41 M, 4.9 mL, 2 mmol) to give a white precipitate. The solvent was evaporated under reduced pressure, and the precipitate was redissolved in a mixture of toluene (15 mL) and ether (2 mL). The solution was allowed to stand at room temperature for 7 days, during which time **3** (0.340 g, 40 %) crystallized as colorless crystals suitable for X-ray crystallographic analysis. M.p.: 190 °C (decomp.).

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